09/926417
Rec'd PCT/PTO 09 NOV 2001
O.Z. 5448

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PATENTE ♦ MARKEN

Antimicrobial copolymers

The invention relates to antimicrobial polymers obtainable by copolymerizing aliphatically unsaturated monomers with amino and ester functions with one or more aliphatically unsaturated amino-functionalized monomers, and to a process for preparing the copolymers, and to their use.

The invention further relates to antimicrobial polymers obtainable by graft-copolymerizing ester- and amino-functionalized aliphatically unsaturated monomers, and to a process for preparing the graft polymers, and to their use.

It is highly undesirable for bacteria to become established or to spread on the surfaces of pipelines, containers or packaging. Frequently, slime layers form and permit sharp rises in microbial populations, and these can lead to persistent impairment of the quality of water, drinks or foods, and even to spoilage of the product and harm to the health of consumers.

Bacteria must be kept away from all fields of life in which hygiene is important. This affects textiles for direct body contact, especially in the genital area, and for the care of the elderly and sick. Bacteria must also be kept away from surfaces of furniture and instruments in wards, especially in areas for intensive care and neonatal care, in hospitals, especially in areas for medical interventions, and in isolation wards for critical cases of infection, and also in toilets.

A current method of treating equipment, or the surfaces of furniture or textiles, to resist bacteria, either when this becomes necessary or else as a precautionary measure, is to use chemicals or solutions or mixtures of these which as disinfectants have fairly broad and general antimicrobial action. Chemical agents of this type act nonspecifically and are frequently themselves toxic or irritant, or form degradation products which are hazardous to health. In addition, people frequently exhibit intolerance to these materials once they have become sensitized.

Another method to counteract surface spread of bacteria is to incorporate substances with antimicrobial action into a matrix.

Tert-butylaminoethyl methacrylate is a commercially available monomer in methacrylate chemistry and is used in particular as a hydrophilic constituent in copolymerizations. For example, EP 0 290 676 describes the use of various polyacrylates and polymethacrylates as a matrix for immobilizing bactericidal quaternary ammonium compounds.

In another technical sector US-A 4 532 269 discloses a terpolymer of butyl methacrylate, tributyltin methacrylate and tert-butylaminoethyl methacrylate. This polymer is used as an antimicrobial paint for ships: the hydrophilic tert-butylaminoethyl methacrylate promotes gradual erosion of the polymer, thus liberating the highly toxic tributyltin methacrylate as antimicrobial agent.

In these applications the copolymer prepared using aminomethacrylates is merely a matrix or carrier substance for added microbicidal agents which can diffuse or migrate out of the carrier substance. Sooner or later polymers of this type lose their effectiveness once the "minimal inhibitory concentration" (MIC) is no longer achieved on the surface. European Patent Applications 0 862 858 and 0 862 859 have disclosed that homo- and copolymers of tert-butylaminoethyl methacrylate, a methacrylate having a secondary amino function, have inherent microbicidal properties. To avoid undesirable resistance phenomena in the microbes, particularly bearing in mind the development of resistance by bacteria known from antibiotics research, systems developed in the future will also have to be based on novel compositions with improved effectiveness.
Antimicrobial terpolymers, which contain amino-functionalized monomers, a high content of ethylene, and optionally further monomers, are known from US 5 208 016.

The object of the present invention is therefore to develop novel polymers having antimicrobial action. These, where appropriate in the form of a coating, should prevent the establishment and spread of bacteria on surfaces.

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Surprisingly, it has now been found that copolymerizing two or more components of aliphatically unsaturated monomers, of which component I has been functionalized by means of ester groups and tertiary amino groups and component II by means of amino groups, or graft-copolymerizing these components on a substrate, gives polymers with a long-lasting microbicidal surface which is not attacked by solvents or by physical stresses and which does not exhibit migration. This makes it unnecessary to use other biocides.

The present invention therefore provides antimicrobial polymers obtained by copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where component I and component II are different from one another.

The present invention also provides a process for preparing antimicrobial polymers obtained by graft-copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where components I and II are different from one another.

The copolymers of the invention are prepared by copolymerizing exclusively components I and II. There is no requirement for the use of other aliphatically unsaturated monomers.

Component I may be composed of aliphatically unsaturated monomers whose ester group has been at least singly amino-functionalized, preferably by means of a tertiary amino group. Particularly preferred monomers for component I are acrylates or methacrylates which have been at least singly functionalized by means of a tertiary amino group. Here, too, the preferred position for the amino group is within the ester function.

The aliphatically unsaturated monomers of components I or II used according to the invention and at least singly functionalized by means of a tertiary amino group may have a hydrocarbon radical of up to 50 carbon atoms, preferably up to 30 carbon atoms, particularly preferably up to 22 carbon atoms. The substituents of the amino group may have aliphatic or vinylic hydrocarbon radicals, such as methyl, ethyl, propyl or acrylic radicals, or cyclic hydrocarbon radicals, such as substituted or unsubstituted phenyl or cyclohexyl radicals having up to 25 carbon atoms. The amino group may also have substitution by keto or aldehyde groups, such as acryloyl or oxo groups. The monomers of component I always contain an ester group.

To achieve a sufficient rate of polymerization, the monomers of components I or II used according to the invention should have a molar mass of less than 900, preferably less than 550 g/mol.

In a particular embodiment of the present invention the components I or II used may comprise aliphatic unsaturated monomers functionalized by means of a tertiary amino group and having the general formula

$$R^1NR^2R^3$$

where R^1: is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3: are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R^2 and R^3 are identical or different,

with the proviso that R^1 in monomers of component I contains an ester group.

The monomers of components I and II must be different. Examples of combinations of monomers of components I and II are given in the examples.

Examples of suitable comonomer building blocks for component I are 2-diethylaminoethyl methacrylate, 2-dimethylaminoethyl methacrylate, N-3-dimethylaminopropylmethacrylamide, 2-diethylaminoethyl acrylate, 2-dimethylaminoethyl acrylate, 3-dimethylaminopropyl acrylate and 3-dimethylamino-2,2-dimethylpropyl acrylate.

Monomers suitable for component II are any aliphatically unsaturated monomers which have at least one amino function. This amino function may be primary, secondary, tertiary or quaternary.

Examples of aliphatically unsaturated monomers with at least one primary amino function are 1-amino-2-propene, N-6-aminohexyl-2-propeneamide, N-3-aminopropylmethacrylamide hydrochloride, 2-aminoethyl methacrylate hydrochloride and 3-aminopropyl vinyl ether.

Suitable comonomer building blocks having at least one secondary amino function, besides the secondary-amino-functionalized acrylates and methacrylates described in European Applications 0 862 858 and 0 862 859, are ethyl 3-phenylmethylamino-2-butenoate, ethyl 3-ethylamino-2-butenoate, ethyl 3-methylamino-2-butenoate, 3-methylamino-1-phenyl-2-propen-1-one, N-4-methylamino-1-anthraquinoyl(2-methyl)acrylamide, N-9,10-dihydro-4-(4-methylphenylamino)-9,10-dioxo-1-anthraquinyl-2-methylpropenamide, propyl 2-hydroxy-3-(3-triethoxysilylpropylamino)-2-propenoate, 1-(1-methyl-ethylamino)-3-(2-(2-propenyl)phenoxy)-2-propanol hydrochloride, ethyl 3-phenylamino-3-methyl-2-butenoate, 1-(1-methylethylamino)-3-(2-(2-propenyloxy)phenoxy)-2-propanol hydrochloride, methyl 2-acrylamido-2-methoxyacetate, methyl 2-acetamidoacrylate, N-tert-butylacrylamide, 2-hydroxy-N-2-propenylbenzamide and N-methyl-2-propenamide.

Examples of aliphatically unsaturated monomers having at least one tertiary amino function are 2-diethylaminoethyl methacrylate, 2-dimethylaminoethyl methacrylate, N-3-dimethylaminopropylmethacrylamide, 2-diethylaminoethyl acrylate, 2-dimethylaminoethyl acrylate, 3-dimethylaminopropyl acrylate and 3-dimethylamino-2,2-dimethylpropyl acrylate.

Other suitable monomeric building blocks are aliphatically unsaturated monomers which have at least one quaternary amino function, e.g. 3-methacryloylaminopropyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium methosulfate, 3-acrylamidopropyltrimethylammonium chloride, trimethylvinylbenzylammonium chloride, 2-acryloyloxyethyl-4-benzoylbenzyldimethylammonium bromide, 2-acryloyloxyethyltrimethylammonium methosulfate, N,N,N-trimethylammoniumethane bromide, 2-hydroxy-N,N,N-trimethyl-3-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniumpropane chloride, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]ammoniumethane methyl sulfate, N,N-diethyl-N-methyl-2-[(1-oxo-2-propenyl)oxy]ammoniumethane methyl sulfate, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]ammoniumethane chloride, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniumethane chloride, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniumethane methyl sulfate and N,N,N-triethyl-2-[(1-oxo-2-propenyl)-amino]ammoniumethane.

The novel antimicrobial copolymers may also be prepared by copolymerizing components I and II on a substrate. This gives a physisorbed coating made of the antimicrobial copolymer on the substrate.

Suitable substrate materials are especially any of the polymeric plastics, such as polyurethanes, polyamides, polyesters and polyethers, polyether block amides, polystyrene, polyvinyl chloride, polycarbonates, polyorganosiloxanes, polyolefins, polysulfones, polyisoprene, polychloroprene, polytetrafluoroethylene (PTFE) or corresponding copolymers or blends, or

also naturally occurring or synthetic rubbers, with or without radiation-sensitive groups. The novel process may also be used on surfaces of objects made from metal, from glass or from wood and surface-coated or otherwise coated with plastic.

In another embodiment of the present invention the antimicrobial polymers may be prepared by graft-polymerizing a substrate with the components I and II. The grafting of the substrate allows covalent linking of the antimicrobial polymer to the substrate. Substrates which may be used are any polymeric material, such as the plastics mentioned above.

Prior to the graft copolymerization, the surfaces of the substrates may be activated by a variety of methods. Any standard method for activating polymer surfaces may be used here, for example the substrate may be activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ-radiation. The surfaces are usefully freed in advance in a known manner from oils, fats or other contamination, using a solvent.

The substrates may be activated using UV radiation in the wavelength range from 170 to 400 nm, preferably from 170 to 250 nm. An example of a suitable radiation source is a Noblelight UV excimer apparatus from HERAEUS, Hanau, Germany. However, mercury vapor lamps are also suitable for substrate activation as long as they emit substantial proportions of radiation in the abovementioned ranges. The exposure time is generally from 0.1 seconds to 20 minutes, preferably from 1 second to 10 minutes.

The activation of the standard polymers with UV radiation may moreover also use a photosensitizer. For this, the photosensitizer, such as benzophenone, is applied to the substrate surface and irradiated. A mercury vapor lamp may again be used here, with exposure times of from 0.1 seconds to 20 minutes, preferably from 1 second to 10 minutes.

According to the invention, the activation may also be achieved by plasma treatment using an RF or microwave plasma (Hexagon, Technics Plasma, 85551 Kirchheim, Germany) in air, nitrogen or argon atmospheres. The exposures times are generally from 2 seconds to 30 minutes, preferably from 5 seconds to 10 minutes. The energy supplied in the case of laboratory devices is from 100 to 500 W, preferably from 200 to 300 W.

Corona devices (SOFTAL, Hamburg, Germany) may also be used for activation. The exposure times in this case are generally from 1 to 10 minutes, preferably from 1 to 60 seconds.

Activation by electrical discharge, electron beam or γ-radiation (e.g. from a cobalt 60 source), and also ozonization, allows short exposure times, generally from 0.1 to 60 seconds.

Substrate surfaces may also be activated by flame treatment. Suitable devices, in particular those with a barrier flame front, can readily be constructed or, for example, purchased from ARCOTEC, 71297 Mönsheim, Germany. They may be operated using hydrocarbons or hydrogen as combustion gas. In all cases it is necessary to avoid damage to the substrate by overheating, and this can readily be ensured if the surface of the substrate facing away from the flame treatment side is in intimate contact with a cooled metal surface. Activation by flame treatment is therefore restricted to relatively thin, sheet-like substrates. The exposure times are generally from 0.1 seconds to 1 minute, preferably from 0.5 to 2 seconds. The flames are exclusively nonluminous, and the distances between the substrate surfaces and the outer side of the flame front are from 0.2 to 5 cm, preferably from 0.5 to 2 cm.

The substrate surfaces activated in this way are coated by known methods, such as dipping, spraying or spreading, with components I and II in solution if desired. Solvents which have proven useful are water and water/ethanol mixtures, but other solvents may also be used as long as they are sufficiently capable of dissolving the monomers and give good wetting of the substrate surfaces. Examples of other solvents are

ethanol, methanol, methyl ethyl ketone, diethyl ether, dioxane, hexane, heptane, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran and acetonitrile. Solutions with monomer contents of from 1 to 10% by weight, for example about 5% by weight, have proven successful in practice and generally give, in a single pass, coherent coatings which cover the substrate surface and have thicknesses which can be more then 0.1 μm.

The graft copolymerization of the monomers (components) applied to the activated surfaces may usefully be initiated by radiation in the short-wave segment of the visible range or in the long-wave segment of the UV range of electromagnetic radiation. For example, the radiation from a UV excimer of wavelengths from 250 to 500 nm, preferably from 290 to 320 nm, is very suitable. Mercury vapor lamps are also suitable here as long as they have substantial proportions of radiation in the abovementioned ranges. The exposure times are generally from 10 seconds to 30 minutes, preferably from 2 to 15 minutes.

A graft copolymerization can also be achieved by a process described in European Patent Application 0 872 512 and based on a graft polymerization of monomer molecules and initiator molecules incorporated by swelling.

Even with grafting on a substrate surface, the antimicrobial copolymers produced by the novel methods from components I and II show microbicidal or antimicrobial behavior.

If the novel process is used directly on the substrate surface without grafting, conventional free-radical initiators may be added. Examples of initiators which may be used are azonitriles, alkyl peroxides, hydroperoxides, acyl peroxides, peroxoketones, peresters, peroxocarbonates, peroxodisulfate, persulfate and any of the usual photoinitiators, such as acetophenones, α-hydroxyketones, dimethylketals and benzophenone. The polymerization may also be initiated thermally or, as already stated, by electromagnetic radiation, such as UV light or γ-radiation.

Use of the modified polymer substrates

The present invention also provides the use of the novel antimicrobial copolymers to produce antimicrobially active products, and the products per se which are produced in this way. The products may comprise polymer substrates modified according to the invention or consist of these. Products of this type are preferably based on polyamides, polyurethanes, polyether block amides, polyesteramides or -imides, PVC, polyolefins, silicones, polysiloxanes, polymethacrylate or polyterephthalates surface-modified using novel polymers.

Examples of antimicrobially active products of this type are in particular machine parts for food processing, components in air-conditioning systems, roofing, items for bathroom and toilet use, kitchen items, components of sanitary equipment, components of cages or houses for animals, recreational products for children, components of water systems, food packaging, operator units (touch panels) of devices, and contact lenses.

The present invention also provides the use, to produce hygiene products or items in medical technology, of the polymer substrates whose surfaces have been modified using novel antimicrobial copolymers. That which has been said above concerning preferred materials applies correspondingly. Examples of hygiene products of this type are toothbrushes, toilet seats, combs and packaging materials. The term hygiene item also includes other objects which may come into contact with a large number of people, such as telephone handsets, stair rails, door handles, window catches, and grab straps and grab handles in public conveyances. Examples of items in medical technology are catheters, tubing, protective or backing films and also surgical instruments.

The novel copolymers or graft polymers may be used anywhere where importance is placed on surfaces with release properties or surfaces which are very free from bacteria, i.e. microbicidal. Examples of application of the novel copolymers are in particular surface coatings, protective paints and other coatings in the following sectors:

Marine: Boat hulls, docks, buoys, drilling platforms, ballast water tanks

Construction: Roofing, basements, walls, facades, greenhouses, sun

protection, garden fencing, wood protection

Sanitary: Public conveniences, bathrooms, shower curtains, toilet items, swimming pool, sauna, jointing, sealing compounds

Requisites for daily life: Machines, kitchen, kitchen items, sponge pads, recreational products for children, food packaging, milk processing, drinking water systems, cosmetics

Machine parts: Air-conditioning systems, ion exchangers, process water, solar-powered units, heat exchangers, bioreactors, membranes

Medical technology: Contact lenses, diapers, membranes, implants

Consumer articles: Automobile seats, clothing (socks, sport clothing), hospital equipment, door handles, telephone handsets, public conveyances, animal cages, cash registers, wall-to-wall carpets, wallpapers.

The following examples are given in order to describe the present invention in greater detail, but are not intended to limit its scope as set out in the patent claims.

<u>Example 1:</u>

6 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 6 ml of 2-diethylaminoethyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

<u>Example 1a:</u>

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus

aureus microbes are now detectable.

Example 1b:

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^3.

Example 2:

8 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 8 ml of 2-dimethylaminoethyl methacrylate (Aldrich) and 80 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.2 g of azobisisobutyronitrile dissolved in 6 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.8 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 150 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 2a:

0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 2b:

0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^4.

Example 3:

5 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 7 ml of 3-dimethylaminopropyl ester acrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 3a:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 3b:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^3.

Example 4:

5 ml of N-3-dimethylaminopropylacrylamide (Aldrich), 8 ml of 2-diethylaminoethyl methacrylate (Aldrich) and 70 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.18 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.6 l of n-hexane, whereupon the polymeric product precipitates.

After filtering off the product, the filter cake is washed with 140 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 4a:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2.

Example 4b:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^4.

~~Example 5:~~

4 g of N-3-dimethylaminopropylmethacrylamide (Aldrich), 5 g of 2-diethylaminoethyl methacrylate (Aldrich), 3 g of methyl methacrylate (Aldrich) and 65 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 5a:

0.05 g of the product from Example 5 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial ~~suspension is removed, and the number of microbes~~

~~in the test mixture is determined. After expiry of this time the number of microbes has~~ reduced from 10^7 to 10^2.

Example 5b:

0.05 g of the product from Example 5 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^3.

Example 6:

4 g of N-3-dimethylaminopropylmethacrylamide (Aldrich), 4 g of 2-diethylaminoethyl methacrylate (Aldrich), 2.5 g of butyl methacrylate (Aldrich) and 65 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 6a:

0.05 g of the product from Example 6 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 6b:

0.05 g of the product from Example 6 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is ~~determined. After expiry of this time the number of~~

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~~microbes has reduced from 10^7 to 10^3.~~

In addition to the microbicidal action described above with respect to cells of Pseudomonas aeruginosa and Staphylococcus aureus, all of the samples also exhibited microbicidal action with respect to cells of Klebsiella pneumoniae, Escherichia coli, Rhizopus oryzae, Candida tropicalis and Tetrahymena pyriformis.